

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 84300929.1

(22) Date of filing: 14.02.84

(51) Int. Cl.³: **C 08 J 9/14**
C 08 L 25/02
/(C08L25/02, 27/12)

(30) Priority: 26.04.83 US 489616

(43) Date of publication of application:
14.11.84 Bulletin 84/46

(84) Designated Contracting States:
BE DE FR GB IT NL

(71) Applicant: MOBIL OIL CORPORATION
150 East 42nd Street
New York New York 10017(US)

(72) Inventor: Murray, James Gordon
9 Lycoming Lane
East Brunswick New Jersey 08816(US)

(72) Inventor: Barile, George Conrad
7 Warner Drive
South Somerville New Jersey 08876(US)

(74) Representative: West, Alan Harry
Mobil Court 3 Clements Inn
London WC2A 2EB(GB)

(64) Process for preparing a styrenic polymer foam.

(67) Preparation of a styrenic polymer in foam form involves incorporating within the styrenic polymer a uniform dispersion of a polymeric nucleating agent which has a weight average molecular weight greater than 10,000 and is insoluble in said styrenic polymer, and foaming the styrenic polymer with a foaming agent to yield a foam having a substantially uniform cell size.

EP 0 124 958 A1

A STYRENIC POLYMER AND A PROCESS OF PREPARING THE SAME

The present invention relates to foamable or foamed styrenic polymers and to a process for the preparation thereof.

In the prior art, foamed polymeric materials have been produced utilizing a variety of techniques. One common method comprises integrating within the polymeric material, which is in the form of beads or pellets, a blowing agent, such as pentane, for example, and subsequently utilizing such expandable beads or pellets to form the desired foamed product by extrusion, cavity molding or any other desired molding process. Another prior art extrusion system for the formation of foamed or cellular polymeric material is what is commonly referred to as a direct injection extrusion operation wherein the blowing agent is injected directly into a molten mass of foamable polymeric material and the desired foam material is extruded, as a sheet or tube, for example, in a single continuous operation. Both prior art systems are largely dependent for successful operation upon the selection of a proper cell size control additive to ensure proper cell size of the final products.

It has now been found that styrenic polymers in foam or foamable form can be produced so that the foam will have a uniform cell size by the incorporation in the styrenic polymer of a finely divided high molecular weight polymer nucleating agent which is insoluble in the styrenic polymer.

According, the invention resides in one aspect in a process of preparing a styrenic polymer in foam form comprising, incorporating within the styrenic polymer a uniform dispersion of a polymeric nucleating agent which has a weight average molecular weight greater than 10,000 and is insoluble in said styrenic polymer and foaming the styrenic polymer with a foaming agent to yield a foam having a substantially uniform cell size.

In a further aspect, the invention resides in a styrenic polymer containing a uniform dispersion of a finely divided polymeric nucleating agent having a weight average molecular weight greater than

10,000, insoluble in said styrenic polymer at least at the temperature employed during creation of a foam cell network in said styrenic polymer by means of a foaming agent.

The high molecular weight polymer used as the nucleating agent herein must be insoluble in the styrenic polymer at least at the temperature of the styrenic polymer at the time of creation of the foam network. By high molecular weight is meant a weight average molecular weight of greater than about 10,000. The nucleating agent can be incorporated within the styrenic polymer during formation of the styrenic polymer, i.e. incorporated therein in-situ. Alternatively, the nucleating agent can be incorporated into the foamable styrenic polymer after the formation of the styrenic polymer. Thus, a foamable preformed styrenic polymer containing the nucleating agent can result either from an in-situ incorporation or from incorporation after the polymer has been formed. In addition, the nucleating agent can be incorporated within the foamable styrenic polymer as an integral process step in the creation of the styrenic foam structure. By this is meant, that sometime during the melt stage of the styrene polymer foam process, the nucleating agent can be dispersed therein.

It is believed that any finely divided high molecular weight polymer which is insoluble in the styrenic polymer, at least at the time of the formation of a foam network by means of a foaming agent, can be employed. These polymeric nucleating agents include the nylons, polycarbonates and polyimides but generally that class of polymers known as fluoroplastics is preferred. By fluoroplastics is meant any plastic based on polymers made from monomers containing one or more atoms of fluorine or copolymers of such monomers with other monomers, the fluorine-containing monomer being in the greatest amount by weight (ASTM D-883). The fluoroplastics contemplated include polytetrafluoroethylene, fluorinated ethylene-propylene copolymers perfluoroalkoxy resins, ethylene-tetrafluoroethylene copolymers and polyvinylidene fluoride. Particularly preferred among the fluoroplastics is polytetrafluoroethylene in powder form. These materials all should have a weight average molecular weight of greater

than 10,000. An especially preferred polymer is a commercially available Teflon powder identified as DuPont DLX 6000 and having a mean particle size of about 0.6 microns.

The foamable polymers used herein are styrenic polymers and preferably are polymers of styrene, p-methylstyrene, alpha-methylstyrene, and any monomer mixtures thereof. Polystyrene and poly(p-methylstyrene) are especially preferred. The polymeric nucleating agent must be present in an amount and in a particle size sufficient to yield an at least substantially uniform fine cell foam in the ultimately foamed styrenic polymer. The amount of nucleating agent generally will range from 0.001 to 0.5% by weight of the styrenic polymer prior to the foaming thereof. An effective mean particle size for the nucleating agent is from 0.1 to 10 microns. Particularly preferred is a mean particle size of about 0.6 microns.

After the subject nucleating agent is effectively incorporated within the selected styrenic polymer, the styrenic polymer can be converted into foam form by any conventional process. Two such foaming processes are disclosed in U.S. Patent Nos. 3,462,006 and 3,444,283. If the nucleating agent is incorporated into the styrenic polymer in-situ any of the techniques for the polymerization of the monomeric material can be employed, such as anionic polymerization, bulk polymerization, emulsion polymerization, solution polymerization and suspension polymerization.

Example I

A mixture of styrene (200 ml), pentane foaming agent (1,000 ml), styrene-butadiene AB block copolymer (0.2 gm-containing 40% styrene and having a molecular weight of 225,000) and Teflon powder (0.2 gm DuPont DLX 7000) was polymerized with 1.5N butyl lithium (1.2 ml) by stirring overnight at room temperature. The product was isolated by filtration and consisted of spherical particles 0.05-0.2 mm in diameter.

This product was expanded by foaming the same in boiling water. The resulting product was a uniform small cell foam product having a bulk density of approximately 3 lbs./ft³. (48 kg/m³)

Example II

The process was repeated but with the exclusion of the Teflon powder. The resulting polymer beads were expanded as in Example I. A non-uniform cell structure was present in the foam product.

Example III

Bulk polymerization of styrene was carried out by heating styrene (180 ml), ethylbenzene (20 ml) and Teflon (0.03 gm DuPont DLX 7000) at 130°C for 6 hours and the resultant mixture devolatilized.

The resulting polymer foamed to a fine cell foam structure after saturating with pentane, without the addition of a separate nucleating agent.

Example IV

Example III was repeated using p-methylstyrene monomer instead of styrene. The resulting polymer foamed to a fine cell foam structure without the addition of a separate nucleating agent.

Example V

As an example of the general process disclosed in U.S. Patent No. 3,482,006 and the incorporation of the fluoroplastic nucleating agent into the melt, polystyrene foam can be prepared as follows: Polystyrene resin pellets are admixed with polytetrafluoroethylene powder having a mean particle size of about 0.6 microns such that the nucleating agent constitutes 0.02% by weight based upon the total weight of the polystyrene being charged. These materials are continuously fed into a hopper of, for example, a 2 1/2 inch (6.4 cm) diameter screw extruder having a length to diameter ratio of 24:1. The extruder is operated at an extrusion rate of about 150 lbs. (68 kg) per hour. By means of extruder barrel heaters, the portion of the extruder barrel surrounding the feedzone of the extruder is maintained at a temperature of about 220°F. (104°C). In the heat plasticizing zone, the pentane injection zone, and the mixing zone, the extruder barrel is maintained at a temperature of about 400° to 450°F. (204 to

232°C). About 5% by weight of pentane, based upon the total weight of resin and nucleating agent, is injected into the polystyrene composition at a point beyond the feed zone where the polystyrene is in a molten condition. The molten mass is then passed through the extruder mixing zone and a cooling zone where it is cooled to 290°-320°F. (143 - 160°C), and then extruded through an annular die orifice as a tubular foamed sheet. The tubular foam is passed about and over a mandrel designed to assist in maintaining a substantially uniform diameter within the extruded foam polymer tube. Thereafter, a knife or other cutting means cuts through one wall of the extruded tube and the same is opened to form a single wide sheet of extruded foam which can thereafter be wound into a roll for subsequent storage or use during thermoformation. The foregoing technique employing the polytetrafluoroethylene nucleating agent yields a fine uniform cell foam structure.

CLAIMS

1. A process of preparing a styrenic polymer in foam form comprising, incorporating within the styrenic polymer a uniform dispersion of a polymeric nucleating agent which has a weight average molecular weight greater than 10,000 and is insoluble in said styrenic polymer, and foaming the styrenic polymer with a foaming agent to yield a foam having a substantially uniform cell size.
2. The process of claim 1 wherein said polymeric nucleating agent is incorporated in said styrenic polymer in-situ during the styrenic polymerization.
3. The process of claim 1 wherein said polymeric nucleating agent is incorporated into said styrenic polymer after the latter is polymerized.
4. The process of claim 1 or claim 2 wherein said polymeric nucleating agent is a homopolymer of a monomer containing one or more fluorine atoms or a copolymer of such a monomer with at least one other monomer, the fluorine-containing monomer being in the greatest amount by weight.
5. The process of claim 4 wherein the nucleating agent is polytetrafluoroethylene.
6. The process of any preceding claim wherein said styrenic polymer is selected from a polymer of styrene, p-methylstyrene, alpha-methylstyrene or any monomer mixture thereof.
7. The process of any preceding claim wherein nucleating agent is present, prior to foaming, in an amount between 0.001 and 0.5% by weight of the styrenic polymer.

8. The process of any preceding claim wherein said nucleating agent has a mean particle size from 0.1 to 10 microns.

9. A styrenic polymer containing a uniform dispersion of a finely divided polymeric nucleating agent having a weight average molecular weight greater than 10,000, insoluble in said styrenic polymer at least at the temperature employed during creation of a foam cell network in said styrenic polymer by means of a foaming agent.

10. The styrenic polymer of claim 9 wherein said nucleating agent has a particle size of 0.1 to 10 microns and is present in an amount of from 0.001 to 0.5% by weight of the styrenic polymer.

2424H



European Patent
Office

EUROPEAN SEARCH REPORT

0124958

EP 84 30 0929

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 8)
X	GB-A-1 143 558 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) * Claims 1-3,6-13; page 1, line 53 - page 2, line 21; page 2, lines 59-73; page 3, lines 13-25; page 3, lines 34-57; example II *	1,3-10	C 08 J 9/14 C 08 L 25/02 // (C 08 L 25/02 C 08 L 27/12)
Y	---	2	
Y	GB-A-1 497 319 (SOCIETA ITALIANA RESINE) * Claims 1,2,6,7 *	1,2	
A	GB-A- 997 356 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) * Claims 1-7,11,12,15; page 2, line 97 - page 3, line 1 * -----	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl. 8) C 08 J
The present search report has been drawn up for all claims			

Place of search
THE HAGUE

Date of completion of the search
30-07-1984

Examiner
HALLEMEESCH A.D.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another
document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or
after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding
document

EPO Form 1503 03/82